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Descripti n

Background of the Invention

This invention relates to anode electrodes and, in particular, to nickel anode electrodes and to methods for making same.

Nickel anode electrodes for molten carbonate fuel cells have suffered in the past from creep and structural stability effects as well as from lack of resistance to sintering during prolonged fuel cell use. The presence of the latter effects, in turn, leads to other undesirable consequences. Thus, the anode structure is found to exhibit changes in its pore spectrum and increased contact resistance with attendant loss of electrical contact. Additionally, the anode structure is found to manifest electrolyte migration due to overlapping pore formation. This, in turn, causes electrolyte creep and wetting of the catalyst.

A variety of attempts have been made to reduce electrode creepage and increase sintering resistance in an effort to reduce or eliminate the above effects. In one such attempt, lithium aluminate has been physically and chemically impregnated into the nickel electrode structure. This technique, however, has not provided satisfactory results; since the ceramic particles incorporated into the structure stay at the metallic surface only and do not act as sites for inhibiting dislocation movements.

Another attempt at reducing electrode creepage and increasing sintering resistance has centered around the use of nickel chromium alloy to provide Cr_2O_3 dispersoids in the electrode structure. Electrodes made in this way have evidenced some short term improvement, but over the long term, the alloy evidences accelerated creep and physical changes due to an unstable internal structure formed by the Cr_2O_3 dispersoids in the nickel metal matrix. While higher chromium levels have resulted in satisfactory creep strength, the formation of an outer growing Cr_2O_3 layer at the expense of the internal oxide dispersoids causes electrolyte wetting and preferential loss of oxides near the gas/metal surface.

Another attempt at reducing creepage and increasing sintering resistance of the anode electrode has been to use nickel aluminum alloys to form an electrode structure stabilized by Al_2O_3 dispersoids. Work in this direction has, however, been very limited due to the difficulties in initial sintering of the nickel aluminum powders.

Researchers have also used metal coated ceramic particles for anode fabrication. The sintering behavior and creep resistance of such structures, however, has not been reported.

Anode structures prepared by the prior techniques have thus not proven satisfactory for one reason or another. It is therefore an object of the present invention to provide a nickel anode structure which evidences less creepage, improved structural stability and increased sintering resistance during use.

Summary of the Invention

The above and other objectives are realized in a method of producing a nickel anode electrode comprising the steps of:

oxidizing a nickel alloy material containing 1 to 5% by weight of alloying material which is selected from the group consisting of aluminum, yttrium, magnesium, titanium, tantalum, molybdenum und cerium to produce in its exterior nickel oxide and in its interior nickel metal throughout which is dispersed an oxide of the alloying material;

and reducing said nickel oxide of said oxidized material to produce nickel metal in the material exterior, whereby a material is formed having nickel metal in its exterior and in its interior nickel metal throughout which is dispersed an oxide of the alloying material;

said oxidation being carried out in an atmosphere containing oxygen at a temperature in a range from about 700 to 1,000 degrees centigrade over a period of time in the range from about one to ten hours; and

said reduction being carried out in an atmosphere containing hydrogen and/or carbon monoxide at a temperature in a range of 600 to 1,000 degrees centigrade over a period of time in the range from one-half to two hours;

and further comprising the step of:

sintering said reduced material,

wherein the oxidation is optionally carried out in two steps separated by a particle diminution or break-up step.

In accordance with the principles of the present invention, a nickel alloy material is subjected to an oxidation treatment under controlled conditions. In particular, these conditions are such as to cause the interior of the material to comprise a nickel metal throughout which is dispersed an oxide of the alloying material. The conditions are also such as to cause the exterior of the material to comprise a nickel oxide layer of a predetermined thickness, preferably equal to or less than about five micrometers.

The oxidized material so formed is then reduced to convert the nickel oxide outer layer to nickel metal. By also sintering the material during the reduction process, a sintered porous anode component is formed having nickel in its exterior and in its interior a metallic nickel matrix throughout which is dispersed an oxide of the alloying material. With this type of configuration for the electrode, the electrode is found to exhibit reduced creepage and increased resistance to sintering during use.

In one embodiment of the invention to be disclosed hereinafter, the oxidation treatment comprises a single oxidation step which results in both the nickel oxide exterior and the nickel metal interior with dispersed alloying oxide. In a second embodiment, the oxidation treatment comprises a first oxidation step, a particle break-up step and a second oxidation step. In this case, the first oxidation step produces both in the interior and exterior of the material a nickel metal having dispersed therethrough an oxide of the alloying material. The second step causes a reduction in the particle size of the oxidized material and th final or second oxi-

dation step converts the exterior of the material to nickel oxide.

Also, in a further aspect of the invention, the electrode resulting from the reduction/sintering process is lithiated under controlled conditions so as to avoid unwanted carbonate electrolyte loss during cell use.

Brief Description of the Drawings

The above and other features and aspects of the present invention will become more apparent upon reading the following detailed description in conjunction with the accompanying drawings, in which:

Figs 1 and 2 show flow diagrams of first and second embodiments of a method for fabricating a nickel anode electrode in accordance with the principles of the present invention;

Fig. 3 portrays the effects of the methods of Figs. 1 and 2 on the nickel alloy particles being processed; and

Fig. 4 shows graphically the voltage and resistance plotted against hours of usage of a molten carbonate fuel cell employing a nickel anode fabricated in accordance with the invention.

Detailed Description

In accordance with the invention, nickel anodes are prepared by the method illustrated in the flow diagrams of Figs 1 and 2. A nickel alloy material containing about one to five weight percent alloying material is used for anode fabrication. The alloying material is one which upon oxidation will provide highly stable oxides in the interior of the anode and is selected from the group consisting of aluminum, yttrium, magnesium, titanium, tantalum, molybdenum and cerium. For the purposes of the present application, the alloy will be assumed to be a Ni-Al alloy powder, and, in particular, a Ni-5Al powder.

After consolidation of the Ni-5Al particles, the particles are subjected to a controlled oxidation treatment. This treatment differs in the Fig. 1 and Fig. 2 embodiments of the invention, as will be discussed at length hereinbelow. However, in both embodiments, the treatments result in particles having an outer layer, which may be total or partial, of nickel oxide of predetermined thickness and an interior comprised of nickel metal having dispersed therethrough Al_2O_3.

Fig. 3 shows in (a) an optical microscope photograph of nickel aluminum particles 10 after the oxidation treatment. As illustrated, the particles in their exteriors contain a NiO layer 11 and in their interiors a nickel metal 12 throughout which is homogeneously dispersed the Al_2O_3 precipitates 13.

Selection of the particular oxidation conditions utilized in the oxidation treatment for a particular case will depend, in part, upon the thickness of the NiO skin desired in the oxidized product. The latter, in turn, will depend upon the thickness needed to permit sintering during formation of the electrode while still achieving required strength. It has been found that a thickness equal to or less than about five µm (micrometers) allows proper sintering and provides good strength. In a particular situation, however, the optimum conditions for achieving the desired thickness can be empirically determined.

After oxidation treatment, the Ni-5Al particles are subjected to a reduction process also under controlled conditions. Preferably, prior to the reduction process, the particles are compacted into a cohesive porous membrane or unitary structure either by conventional compression in a mold or by conventional liquid tape casting. The resultant compact may typically be 0.76 to 1.52 mm (30 to 60 mils) thick, and 50 to 60 percent porous. Thinner compacts are usable to form flat electrode membranes, while thicker compacts are usable to form corrugated electrode membranes. Although formation of the compact is preferably carried out after oxidation, formation prior to oxidation is also possible.

The reduction of the compact is furthermore carried out in a manner which simultaneously results in sintering of the compact. More particularly, th compact is subjected to a hydrogen atmosphere under preselected pressure and temperature conditions. These conditions are such that the NiO out r layer of each particle is reduced to metallic nickel which covers all or part of the particle surface. As a result, the particles take on a partial or full nick l exterior and the latter promotes the sintering process which also occurs as a result of the heat and pressure being applied. Conditions for the reduction/sintering are a temperature in the range of 600 to 1,000 degrees centigrade and a period of time from one-half to two hours.

In (b) of Fig. 3 joined particles resulting from the reduction and sintering are shown. As illustrated, a strong neck area 21 is formed between the resultant reduced Ni outer layers 22 of the two particles. The interiors of the particles, in turn, still contain Al_2O_3 particles 23 homogeneously dispersed within the nickel metal 24 as displayed in the higher magnification scanning electron microscope photograph of Fig. 3 (c).

The resultant anode structure thus contains nickel metal either as an outer layer or as a partial covering, and an interior composed of Al_2O_3 finely dispersed within a nickel matrix. The anode structure so formed has been found to exhibit superior strength and resistance against physical creepage during use. This is believed, in part, attributable to the interior homogeneous in-situ precipitated Al_2O_3 particles which are smaller than 1 µm (submicron size) and which are highly effective in pinning the dislocation movements which occur as a result of sintering during use.

Additionally, sintering during the reduction phase is more readily enabled by the Ni at the outer surfaces. This nickel covering also provides the resultant anode with a non-wettable surface and thus one less susceptible to electrolyte creep.

As shown, the oxidation treatment in the embodiment of FIG. 1 comprises a single oxidation step during which both the formation of the NiO outer layer and the inner nickel metal with dispersed Al_2O_3 occurs. The conditions of this treatment are such that internal Al_2O_3 precipitates are formed as oxygen diffuses into the Ni-Al alloy particles and oxidizes

the aluminum. The conditions are also such that either simultaneously with or subsequent to th oxidation of the aluminum, nickel diffuses out of the particles to combine with oxygen to form a NiO outer layer or skin. The result is as mentioned above and shown in (a) of FIG. 3, nickel particles with a NiO outer layer and a nickel metal interior with Al_2O_3 dispersed therethrough.

The above single oxidation step is preferably carried out at a temperature within the range of 700-1,000 degrees centigrade for a time from about 1 to 10 hours. If the atmosphere used is air or pure oxygen only, the oxidation of the aluminum and nickel will occur simultaneously. If, however, the atmosphere is initially a water vapor/hydrogen mixture, possibly diluted with nitrogen or a carbon dioxide/carbon monoxide mixture, and this initial atmosphere is followed by an atmosphere of air or pure oxygen only, the oxidation of the aluminum can be made to occur and be completed first and subsequently the oxidation of the nickel will occur. An example of conditions resulting in the latter, is use of an initial atmosphere containing water vapor and hydrogen having a ratio of partial pressures of about 100 for about 10 hours at 950 degrees centigrade, followed by an atmosphere of pure oyxgen for about 10 to 30 minutes. An example of the simultaneous case, on the other hand, is use of an air atmosphere for about three hours at a temperature of 900 degrees centigrade.

In the embodiment of the invention shown in Fig. 2, the oxidation treatment comprises two oxidation steps separated by a particle diminution or break-up step. This treatment results in an anode structure of smaller mean pore size than the treatment in Fig. 1 and is preferable in cases where a small mean pore size is desired.

In this case, the initial oxidation conditions are such that internal oxidation of the aluminum in the particles occurs first. In particular, aluminum oxide is precipitated as small Al_2O_3 dispersoids which are smaller than 1 µm (sub-micron) with larger concentrations of the dispersoids being present at the particle grain boundaries owing to the larger concentrations of aluminum. The initial conditions are also such that no oxidation of the nickel takes place. Thus, this oxidation step results in a nickel metal matrix throughout which aluminum oxide dispersoids are homogeneously distributed, with a larger concentration of dispersoids at the particle grain boundaries.

Following the initial oxidation, the resultant particles are fractured at the grain boundaries by a particle diminution or break-up step which is typically accomplished by milling. This process subjects the particles to extreme stresses causing fracture primarily at the grain boundaries where an excess of the aluminum oxide dispersoids have introduced considerable internal stresses.

After milling, the reduced in size particles are now subjected to a second controlled oxidation step. In this step the conditions are such that nickel diffuses out of the particles and combines with oxygen to form the desired NiO outer layer or skin.

A consequence of the aforesaid nickel oxide formation at the surface of the particles is the exfoliation of any residual Al_2O_3 accumulations that existed at the grain boundaries and that are now at the surfaces of the smaller particles. An Al_2O_3 surface layer would greatly hinder the subsequent sintering of the particles, but the growth of the nickel oxide layer from below serves the dual purpose of spalling off the Al_2O_3 and providing for an easily sinterable material upon reduction.

The conditions in the first oxidation step and the second oxidation step of the FIG. 2 embodiment are like those for the FIG. 1 oxidation treatment where that treatment is carried out serially, i.e., where the aluminum is first oxidized completedly and then the nickel is oxidized. In particular, the first step has conditions like those present in the aluminum oxidation portion of the serially carried out FIG. 1 oxidation treatment and the second step conditions like those present in the nickel oxidation portion of such serial FIG. 1 oxidation treatment.

Accelerated creep tests have been performed on anodes made in accordance with the invention and have confirmed their superior strength. Thus, anodes of the invention crept less than one percent under conditions where ceramic impregnated nickel anodes crept 20 per cent and the NiCr anodes crept approximately 3-5 per cent. Cell testing has also confirmed dimensional stability of the nickel anodes and electrochemical performance close to state-of-the-art has been observed. In this regard, FIG. 4 shows the voltage and resistance plotted against hours of operation of a molten carbonate fuel cell employing an anode constructed in accordance with the invention. As can be seen, the cell provided a 712mv output at a current density of 160mA/cm² with a 75 percent fuel utilization and a 50 percent oxidant utilization.

It should be noted that the oxidation of the nickel alloy of the latter cell was carried out at a temperature of about 900 degrees centigrade which resulted in substantially complete oxidation of the aluminum to Al_2O_3. Such complete oxidation is believed preferable, although less than complete oxidation at lower temperatures results in a usable anode, but one whose resistance characteristic is higher and voltage is lower than in the complete oxidation case.

It should also be noted that the pore size of the resultant anode is dependent upon the size of the nickel alloy particles being processed. Commercially made Ni-5Al particles have been found to be large, and typically result in a mean pore size for the anode of between 20–25 µm (micrometers). If smaller pore sizes are desired, the process of Fig. 2 whereby milling of the particles after oxidation of the aluminum only can be followed. A pore size for the anode between 5 to 6 µm (micrometers) is preferable and this can be realized by milling the particles to a size of 3 to 10 µm (micrometers).

Another technique for providing reduced pore size in the anode structure is to impregnate the structure after sintering with fine ceramic particles such as, for example, $LiAlO_2$. This will not alter the conductivity or activity of the electrode, but will provide the desired pore size reduction, as well as increased wettability and electrolyte retention dur-

ing use.

In a further aspect of the present invention, the anode structure as formed above is further treated by a lithiation process so that use of the anode in a molten carbonate fuel cell does not cause loss of molten carbonate electrolyte. More particularly, it has been found that the Al_2O_3 dispersoids in the anode structure react with the lithium in the lithium carbonate/potassium carbonate electrolyte melt. This results in the conversion of some or all of the Al_2O_3 dispersoids to $LiAlO_2$. Commensureate with the Al_2O_3 to $LiAlO_2$ conversion the ratio of lithium to potassium cations in the carbonate electrolyte melt decreases.

In accordance with this aspect of the invention, these effects are prevented by a lithiation treatment applied to the anode electrode prior to its use. This process adds sufficient lithium to the anode to enable the subsequent Al_2O_3 to $LiAlO_2$ conversion to occur without affecting the electrolyte cation balance.

More particularly, this lithiation procedure is carried out by precipitation of stoichiometric to 20 percent excess quantities of lithium salt, such as lithium hydroxide, onto the surface of the nickel particles of the anode. The anode is then subjected to heat treatment to promote reaction conversion of Al_2O_3 to $LiAlO_2$. Heat treatment is accomplished in a reducing atmosphere containing at least 3 percent hydrogen and at a temperature of greater than 730 degrees centigrade. The atmosphere should also be entirely free of carbon dioxide.

Heat treatment times for the lithiation can be quite lengthy, or short, depending upon the degree of conversion required. All or some conversion may take place during the heat treatment but regardless of the extent, the lithium content is available for future conversion in the fuel cell.

In all cases, it is understood that the above-described arrangements are merely illustrative of the many possible specific embodiments which represent applications of the present invention. Thus, for example, while the sintering of the compact was described as occurring simultaneously with the reduction procedure, it may also be carried out after the reduction procedure is completed. Furthermore, formation of the particles into a compact may occur after reduction, if sintering is also performed after reduction. Also, it should be noted that the oxidation treatment and the subsequent reduction and sintering procedure can be carried out in a common furnace by suitable control of the atmospheric and heating conditions to produce the desired treatments.

Claims

1. A method of producing a nickel anode electrode comprising the steps of:
oxidizing a nickel alloy material containing 1 to 5% by weight of alloying material which is selected from the group consisting of aluminum, yttrium, magnesium, titanium, tantalum, molybdenum und cerium to produce in its exterior nickel oxide and in its interior nickel metal throughout which is dispersed an oxide of the alloying material;
and reducing said nickel oxide of said oxidized material to produce nickel metal in the material exterior, whereby a material is formed having nickel metal in its exterior and in its interior nickel metal throughout which is dispersed an oxide of the alloying material;
said oxidation being carried out in an atmosphere containing oxygen at a temperature in a range from about 700 to 1,000 degrees centigrade over a period of time in the range from about one to ten hours; and
said reduction being carried out in an atmosphere containing hydrogen and/or carbon monoxide at a temperature in a range of 600 to 1,000 degrees centigrade over a period of time in the range from one-half to two hours;
and further comprising the step of:
sintering said reduced material,
wherein the oxidation is optionally carried out in two steps separated by a particle diminution or break-up step.

2. A method in accordance with claim 1 wherein:
said nickel alloy material is initially in particle form,
and further comprising the steps of:
compacting said particles to form a porous cohesive structure, said compacting occurs one of:
before said oxidizing; after said oxidizing and before said reduction; and after said reduction;
and sintering said compact one of: after said reduction; and simultaneously with said reduction.

3. A method in accordance with claim 2 wherein:
the size of said particles is in the range of 3 to 10 μm at the time of reduction.

4. A method in accordance with claim 1 further comprising:
impregnating the material with ceramic particles after reduction.

5. A method in accordance with claim 4 wherein:
said ceramic is $LiAlO_2$.

6. A method in accordance with claim 1 wherein:
said oxidizing step includes:
a first oxidation carried out for about 10 hours at 950°C in an atmosphere comprising water vapor and hydrogen having a ratio of partial pressures of about 100 so as to cause oxidation of said alloying material only;
a second oxidation subsequent to said first oxidation carried out in an atmosphere of pure oxygen for about 10 to 30 minutes to cause oxidation of said nickel.

7. A method in accordance with claim 6 further comprising:
subjecting said material after said first oxidation and prior to said second oxidation to a material diminution step.

8. A method in accordance with claim 1 wherein:
the nickel oxide exterior comprises a layer of thickness equal to or less than 5 μm.

9. A method in accordance with claim 8 wherein:
said layer is a partial layer.

10. A method in accordance with claim 1 further comprising:
precipitating a lithium salt onto said sintered material;
heating said material after said precipitation.

11. A method in accordance with claim 2 wherein: said reduction and sintering occur simultaneously.

12. An anode electrode made by the method of claim 1, 2, 6 or 8.

Patentansprüche

1. Verfahren zur Herstellung einer Nickelanodenelektrode, umfassend die Stufen:
Oxidieren eines Nickellegierungsmaterials enthaltend 1 bis 5 Gew.-% an Legierungsmaterial, welches ausgewählt ist aus der Gruppe bestehend aus Aluminium, Yttrium, Magnesium, Titan, Tantal, Molybdän und Cer, um in seinem äußeren Bereich Nickeloxid und in seinem inneren Bereich Nickelmetall, in welchem durchweg ein Oxid des Legierungsmaterials dispergiert ist, zu erzeugen;
und Reduzieren des Nickeloxids des oxidierten Materials, um in dem äußeren Bereich des Materials Nickelmetall zu erzeugen, wobei ein Material gebildet wird, das in seinem äußeren Bereich Nickelmetall und in seinem inneren Bereich Nickelmetall, in welchem durchweg ein Oxid des Legierungsmaterials dispergiert ist, enthält;
wobei die Oxidation in einer Sauerstoff enthaltenden Atmosphäre bei einer Temperatur im Bereich von etwa 700 bis 1000°C während eines Zeitraums im Bereich von etwa 1 bis 10 Stunden durchgeführt wird; und
die Reduktion in einer Wasserstoff und/oder Kohlenmonoxid enthaltenden Atmosphäre bei einer Temperatur im Bereich von 600 bis 1000°C während eines Zeitraums im Bereich von 1/2 Stunde bis 2 Stunden durchgeführt wird;
sowie umfassend die weitere Stufe:
Sintern des reduzierten Materials,
wobei die Oxidation gegebenenfalls in zwei Stufen durchgeführt wird, die durch eine Teilchenverkleinerungs- oder vermahlungsstufe getrennt sind.

2. Verfahren nach Anspruch 1, worin das Nickellegierungsmaterial zu Beginn in Teilchenform vorliegt, umfassend die weiteren Stufen:
Verdichten der Teilchen unter Bildung einer porösen zusammenhängenden Struktur, wobei das Verdichten entweder vor dem Oxidieren, nach dem Oxidieren und vor der Reduktion oder nach der Reduktion erfolgen kann;
und Sintern des verdichteten Materials entweder nach der Reduktion oder gleichzeitig mit der Reduktion.

3. Verfahren nach Anspruch 2, worin die Größe der Teilchen zur Zeit der Reduktion im Bereich von 3 bis 10 µm liegt.

4. Verfahren nach Anspruch 1, welches zusätzlich das Imprägnieren des Materials mit keramischen Teilchen nach der Reduktion umfaßt.

5. Verfahren nach Anspruch 4, worin das keramische Material $LiAlO_2$ ist.

6. Verfahren nach Anspruch 1, worin die Oxidationsstufe umfaßt:
eine erste Oxidation, di während etwa 10 Stunden bei 950°C in einer Wasserdampf und Wasserstoff in einem Verhältnis der Partialdrücke von etwa 100 umfassenden Atmosphäre durchgeführt wird, um lediglich die Oxidation des Legierungsmaterials zu bewirken;
eine zweite, auf di erste Oxidation folgende Oxidation, welche in einer Atmosphäre von reinem Sauerstoff während etwa 10 bis 30 Minuten durchgeführt wird, um die Oxidation des Nickels zu bewirken.

7. Verfahren nach Anspruch 6, welches weiterhin eine Materialverkleinerungsstufe nach der ersten Oxidation und vor der zweiten Oxidation umfaßt.

8. Verfahren nach Anspruch 1, worin der äußere Nickeloxidbereich eine Schicht einer Dicke von 5 µm oder darunter umfaßt.

9. Verfahren nach Anspruch 8, worin die Schicht eine Teilschicht ist.

10. Verfahren nach Anspruch 1, welches weiter umfaßt:
Ausfällen eines Lithiumsalzes auf das gesinterte Material;
Erhitzen des Materials nach der Ausfällung.

11. Verfahren nach Anspruch 2, worin die Reduktion und das Sintern gleichzeitig erfolgen.

12. Anodenelektrode, hergestellt nach dem Verfahren von Anspruch 1, 2, 6 oder 8.

Revendications

1. Procédé de fabrication d'une anode en nickel consistant en les stades suivants:
oxyder un alliage de nickel renfermant de 1 à 5% en poids de matériau d'alliage choisi parmi aluminium, yttrium, magnésium, titane, tantale, molybdène et cérium, pour produire à sa surface de l'oxyde de nickel et à l'intérieur du nickel métallique dans lequel est dispersé un oxyde du matériau d'alliage;
et réduire ledit oxyde de nickel dudit matériau oxydé pour donner du nickel métallique à la surface du matériau, un matériau étant ainsi formé qui possède du nickel métallique en surface et, à l'intérieur, du nickel métallique dans lequel est dispersé un oxyde du matériau d'alliage;
ladite oxydation étant réalisée dans une atmosphère renfermant de l'oxygène à une température se situant entre environ 700 et 1000 degrés centigrades sur une période de temps allant d'environ une à dix heures; et
ladite réduction étant réalisée dans une atmosphère contenant de l'hydrogène et/ou du monoxyde de carbone à une température dans un intervalle de 600 à 1000 degrés centigrades sur une période de temps allant d'une demi-heure à deux heures;
et consistant en outre en:
un frittage dudit matériau réduit;
l'oxydation étant éventuellement effectuée en deux stades séparés par un stade de réduction ou broyage des particules.

2. Procédé selon la revendication 1 où:
ledit matériau d'alliage de nickel est initialement sous forme de particules,
le procédé comprend en outre les stades qui consistent à:
compacter lesdites particules pour former une structure cohérente poreuse, ledit compactage se produisant: avant ladite oxydation; après ladite oxydation et avant ladite réduction; ou après ladit ré-

duction;
et fritter ledit compact après ladite réduction; ou en mêm temps que ladite réduction.

3. Procédé selon la revendication 2 où:
la taille desdites particules se situe dans l'intervalle de 3 à 10 µm au moment de la réduction.

4. Procédé selon la revendication 1 comprenant en outre:
l'imprégnation du matériau à l'aide de particules céramiques après réduction.

5. Procédé selon la revendication 4 où:
ladite céramique est $LiAlO_2$.

6. Procédé selon la revendication 1 où:
ledit procédé d'oxydation comprend:
une première oxydation effectuée durant environ 10 heures à 950°C en atmosphère formée de vapeur d'eau et d'hydrogène dans un rapport de pressions partielles d'environ 100 de manière à provoquer l'oxydation dudit matériau d'alliage seulement;
une seconde oxydation faisant suite à ladite première oxydation et réalisée dans une atmosphère d'oxygène pur pendant environ 10 à 30 minutes pour provoquer l'oxydation du nickel.

7. Procédé selon la revendication 6 comprenant en outre le fait de
soumettre ledit matériau, après ladite première oxydation et avant ladite seconde oxydation, à un stade de réduction du matériau.

8. Procédé selon la revendication 1 où:
ladite surface extérieure d'oxyde de nickel comprend une couche d'épaisseur égale ou inférieure à 5 µm.

9. Procédé selon la revendication 8 où:
ladite couche est une couche partielle.

10. Procédé selon la revendication 1 comprenant en outre:
la précipitation d'un sel de lithium sur ledit matériau fritté;
le chauffage dudit matériau après ladite précipitation.

11. Procédé selon la revendication 2 où:
la réduction et le frittage se produisent simultanément.

12. Anode fabriquée par le procédé des revendications 1, 2, 6 ou 8.

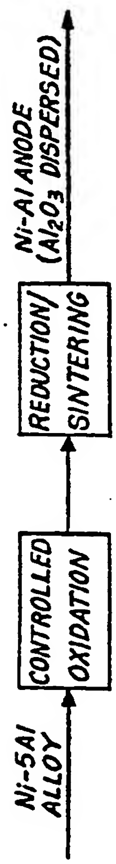

FIG. 1

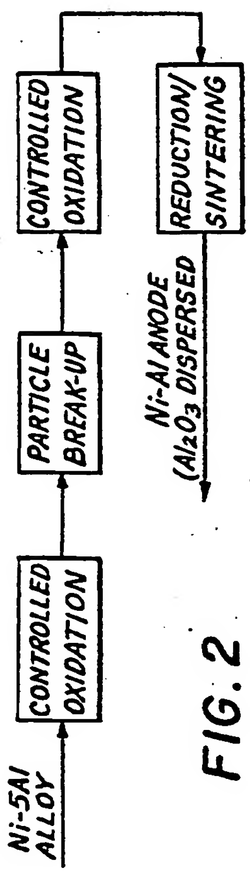

FIG. 2

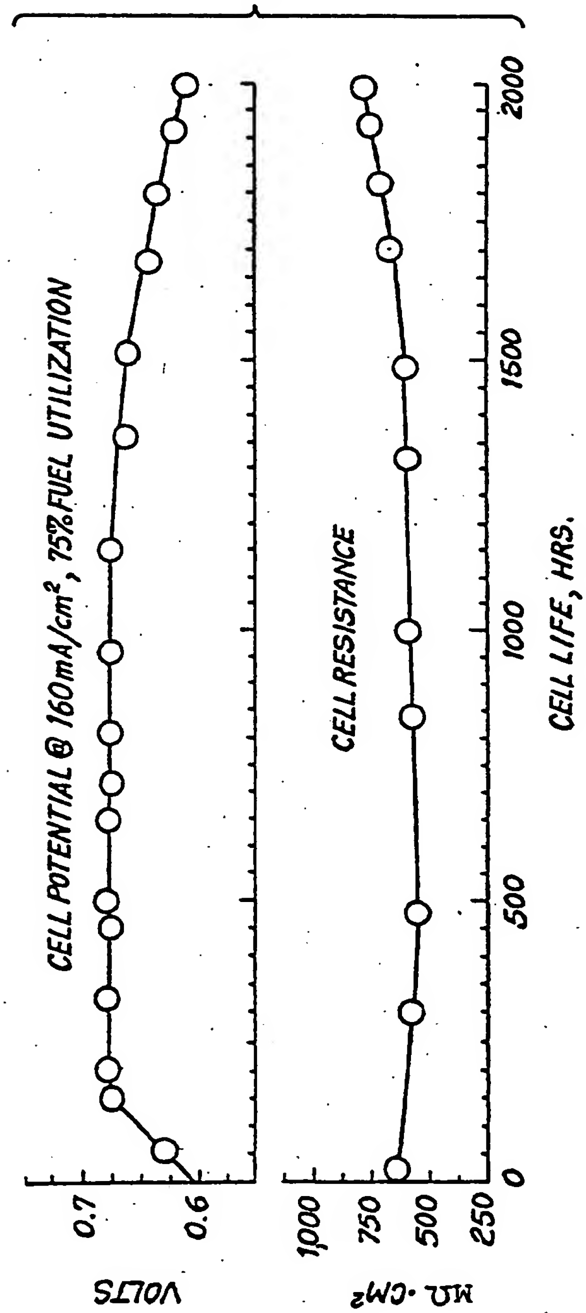

FIG. 4

(a) OXIDIZED

(b) OXIDIZED / REDUCED

(C) OXIDIZED / REDUCED – MAGNIFIED

FIG. 3